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TI Observations on the ionic composition of blue-green algae growing in saline lagoons
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SO Proc. Natl. Inst. Sci. India, (19550000) vol. 21, no. 2, pp. 90-102.

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SO European Journal of Phycology, (Oct., 1999) Vol. 34, No. 4, pp. 393-403.

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ON THE COVER: Fault scarp produced by October 28, 1983, earthquake, west side of Lost River Range, central Idaho. View is east toward Borah Peak, from north side of Rock Creek. Scarp, with about 3 m of vertical separation, cuts Quaternary gravel terrace of Rock Creek. Irrigation ditch shows minor left-lateral separation. Intersection of line along bottom of ditch and fault plane forms "piercing point" in fault plane, which can be used to determine net slip of fault. Photo by Paul Karl Link.

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Calcification of cyanobacterial mats in Solar Lake, Sinai

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ABSTRACT

Pore-water samples were obtained from the shallow-water part of Solar Lake (Sinai) where luxurious cyanobacterial mats grow. These samples were analyzed for Ca^{2+}, Mg^{2+}, Sr^{2+}, Cl^-, SO_4^{2-}, and titration alkalinity (TA) to determine the role of cyanobacterial growth and degradation on the calcification of the mats. The data are modeled thermodynamically to predict mineral–pore-water equilibria. Our data support earlier bacterial and sedimentological studies suggesting that the degradation of the cyanobacterial mat via sulfate reduction is of major importance in the calcification process.

INTRODUCTION

Stromatolites are organosedimentary structures produced through the growth and degradation of microorganisms, principally cyanobacteria (Walter, 1976). Several mechanisms of the production of $CaCO_3$ within these organisms and the lithification of the stromatolitic structure have been proposed. Black (1933) suggested that the cyanobacteria act as sediment binders and simply trap $CaCO_3$ sediment introduced into the environment from another source. Changes in pH due to photosynthetic activity of the cyanobacteria have been proposed as the major factor in $CaCO_3$ precipitation (Dalrymple, 1965). Bacterial degradation of algal material below the zone of photosynthesis has also been advanced as a major factor in $CaCO_3$ formation (Krumbein and Cohen, 1977). The dissolution of authigenic gypsum as bacterially mediated sulfate reduction proceeds and the subsequent precipitation of $CaCO_3$ have also been suggested to be important in hypersaline environments (Friedman and Sanders, 1978). The delineation of which mechanism(s) is (are) important in the calcification process may be better understood by the study of the pore-water geochemistry of cyanobacteria-rich modern sediments.

We present pore-water data from the sediments of Solar Lake, Sinai, a hypersaline lake occupied by a luxurious cyanobacterial mat, which can be interpreted to indicate that the third proposed mechanism, the decomposition of the mat material via sulfate reduction, is of utmost importance in the calcification process at this location.

METHODS

Cores were taken manually in water depths of less than 0.7 m in Solar Lake using an 8-cm (interior diameter) polycarbonate core liner. The core was placed into a N_2-flushed polyvinyl chloride core carrier and returned to the Steinitz Marine Biological Station in Elat, Israel. The core was placed into a N_2-flushed glove bag, sectioned and centrifuged under N_2 to remove the pore fluids. The centrifugation was accomplished at in situ bottom-water temperatures.

Chloride was determined via micro-Mohr titration. Calcium, magnesium, and strontium analyses were performed via atomic absorption spectrophotometry. The Mg^{2+}, Ca^{2+}, and Sr^{2+} samples were diluted with a potassium and lanthanum matrix solution. Standards and blanks were made up in the same matrix solution. Titration alkalinities were determined by the addition of 0.1515 N HCl. Reactive silicate was analyzed colorimetrically on acidified samples utilizing Auto-Analyzer techniques after dilution with distilled-deionized water. Sulfate was determined using the technique of Howarth (1978) with modifications for higher SO_4^{2-} concentrations. The pH was measured by inserting the electrode directly into the sediment (Fisher and Matisoff, 1981). The pore-water chemistry was thermodynamically modeled using the program of Long and Angino (1977) for high-ionic-strength solutions.

PREVIOUS WORK

The biology of the cyanobacterial mats and the limnology of Solar Lake are well documented (Cohen et al., 1977a, 1977b, 1977c; Krumbein et al., 1977; Jørgensen and Cohen, 1977). Photosynthetic rates in the shallow-water mats where our cores were obtained averaged $10\ g \cdot m^{-2} \cdot d^{-1}$ (Krumbein et al., 1977). However, more than 99% of this organic matter is later mineralized (Krumbein et al., 1977) because of very rapid rates of sulfate reduction (Jørgensen and Cohen, 1977).

$CaCO_3$ is found only below 3–5 cm in the mats (Krumbein and Cohen, 1977; Krumbein, 1978), increasing with depth from less than 10% in the top 10 cm to values as high as 80% at 80 cm (Krumbein et al., 1977). Aragonite, low- and high-magnesium calcite, monohydrocalcite, and dolomite have all been observed (Friedman et al., 1973; Krumbein and Cohen, 1977; Aharon et al., 1977). Extensive sedimentological, mineralogical, microbiological, and isotopic studies of these sediments have yielded much data. Therefore, many observations and interpretations regarding the calcification of the cyanobacterial mats have been presented: (1) Calcification of the cyanobacterial mat is currently occurring (Friedman et al., 1973; Krumbein, 1978; Krumbein et al., 1977, Friedman and Foner, 1982). (2) Dolomite is currently forming in these sediments at the expense of aragonite (Aharon et al., 1977). In most cases the dolomite is found in the deepest part of the lake in association with gypsum. However, measurable amounts of dolomite have been observed at depths of ~30 cm in the shallow-water matted sediments along the edge of the lake (Aharon et al., 1977) where no gypsum occurs (Krumbein et al., 1977). (3) A decrease of organic carbon and an increase of inorganic carbon occurs with depth in these shallow-water matted sediments, thought to be due to bacterially mediated conversion of the former to the latter (Krumbein et al., 1977). (4) There is no source of detrital carbonates for the lake sediments.

Despite this generally accepted information, problems exist regarding interpretations of the available data on Solar Lake. For example:

1. The carbon-isotope evidence suggests that the aragonite found in the sediments is produced primarily by the evaporation of seawater, and the calcite is produced by the degradation of organic matter (Aharon et al., 1977). However, the microbiological studies indicate that much of the aragonite appears to be produced either directly or indirectly by microbial processes (Krumbein and Cohen, 1977; Krumbein et al., 1977).

2. The difference of carbon isotopes between aragonite and calcite in the sediments is thought to be due, in part, to the large isotopic difference between the inorganic carbon in the lake water and the organic carbon in the cyanobacterial mat (Aharon et al., 1977), yet recent work indicates that the organic matter in the mat is extremely enriched in ^{13}C ($\delta^{13}C$ = –5), relative to other types of aquatic organic

matter and other cyanobacterially derived organic carbon (Stuermer et al., 1978; Schidlowski, 1983). Thus, the explanation of the $\delta^{13}C$ distribution between the various carbon pools may be enigmatic.

3. SEM photographs indicate the dissolution of diatomaceous material in these sediments (Krumbein, 1978), whereas in situ experiments with quartz beads show no evidence of dissolution (Friedman and Foner, 1982).

RESULTS AND DISCUSSION

Representative pore-water Cl^-, Mg^{2+}, and Ca^{2+} and Mg^{2+}/Cl^-, Ca^{2+}/Cl^- are seen in Figure 1. Our pH data shown in Table 1 compare quite well with the measurements of Krumbein et al. (1977) and Friedman and Foner (1982). The Ca^{2+}/Cl^- ratio decreases across the sediment-water interface to a depth of 25 cm. In this zone, $CaCO_3$ is being precipitated. The Sr^{2+}/Cl^- profile mimics the Ca^{2+}/Cl^- profile, suggesting that some of the $CaCO_3$ being produced is aragonite. As sulfate reduction proceeds, HCO_3^- is produced from the oxidation of organic matter (Berner et al., 1970). This pore-water HCO_3^- can then react with Ca^{2+} to precipitate authigenic carbonate minerals.

The pore-water titration alkalinity (TA) values ranged from 5.26 to 9.09 meq L^{-1}, with maximum values in the top 30 cm (Table 2). Although higher than overlying Solar Lake water values by a factor of 2 to 4, these values are much lower than expected from the measured sulfate reduction rates, suggesting removal via $CaCO_3$ precipitation. The mean sulfate reduction rate in the upper 10 cm of these mats is greater than 100 nmol · cm^{-3} · d^{-1} (Jørgensen and Cohen, 1977). This would yield a HCO_3^- production rate of over 280 μmol · L^{-1} · d^{-1} or over 98 mmol · L^{-1} · yr^{-1} considering a sediment porosity of 70% (Krumbein and Cohen, 1977). This is the equivalent production of 41 μmol · g^{-1} yr^{-1} of $CaCO_3$ if there was a 100% conversion of bacterially produced HCO_3^- to $CaCO_3$. This value can be compared to the potential production of 20 mmol of $CaCO_3$ g^{-1} yr^{-1} if all the carbon that is fixed photosynthetically in the shallow-water mats is converted via diagenesis to $CaCO_3$ (Krumbein et al., 1977). Less than 1% of the fixed carbon in the Solar Lake mats is later converted to calcium carbonate, supporting the results of Krumbein et al. (1977). We have neglected the alkalinity contribution of bisulfide ion; it could be greater than 3 meq L^{-1} in these pore waters (Krumbein and Cohen, 1977), hence reducing the HCO_3^- concentration even lower than the above predicted values. Therefore, HCO_3^- formation via sulfate reduction seems a logical means for the production of the authigenic $CaCO_3$ in these sediments.

Thermodynamic modeling is consistent with $CaCO_3$ production within the mats by showing that the pore waters are indeed supersaturated with respect to calcite but are undersaturated with respect to aragonite in the top 25 cm and at 79 cm (Table 2). This may indicate that the initial locally precipitated aragonite is later dissolved as the dense brine sinks and moves downward through the mat.

In the top 25 cm the Mg^{2+}/Cl^- ratio is greater than the overlying water value. Friedman et al. (1973) observed a similar Mg/Cl enrichment and a Ca/Cl depletion relative to seawater. The Ca^{2+} removal and Mg^{2+} addition in the pore waters in this zone produces Mg^{2+}/Ca^{2+} ratios much greater than can be explained by simple seawater evaporation and the precipitation of $CaSO_4 \cdot 2H_2O$. An additional source of Mg^{2+} is needed, and no gypsum has been detected in the mat community (Krumbein and Cohen, 1977). This input of Mg^{2+} into the pore fluids at these shallow depths may be due either to the degradation of organic matter, as suggested by Friedman et al. (1973), or possibly the diagenetic conversion of high-Mg calcite to low-Mg calcite. As sulfate reduction proceeds, the cyanobacterial mats are degraded and Mg^{2+} from the chlorophyll of these algae is solubilized into the pore fluids.

The chemical modeling results indicate that the pore waters are undersaturated with respect to gypsum (Table 1). Our X-ray diffraction

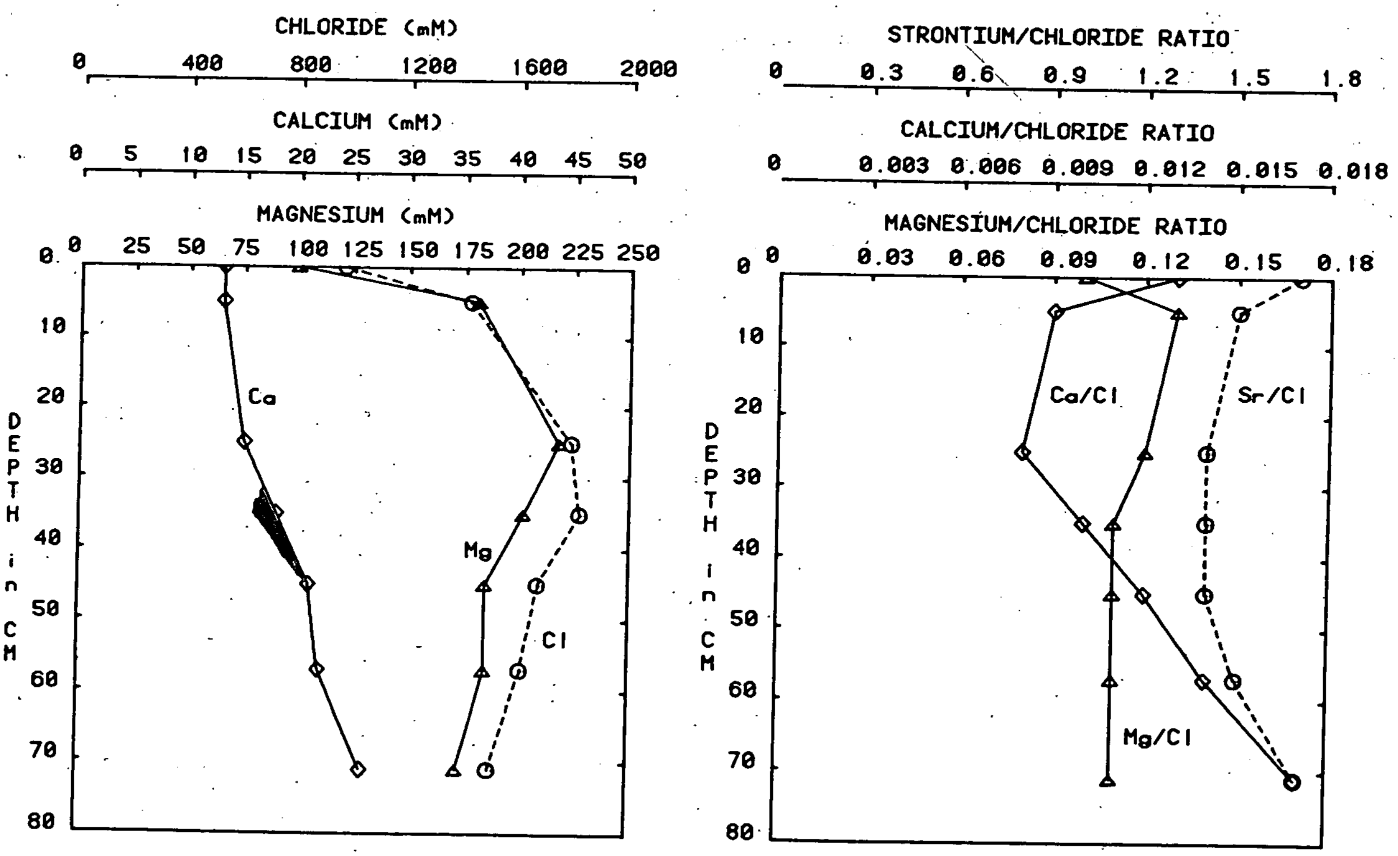

Figure 1. Profiles of pore-water chloride, calcium, and magnesium vs. depth and Sr^{2+}/Cl^-, Ca^{2+}/Cl^-, and Mg^{2+}/Cl^- vs. depth for Solar Lake.

TABLE 1. THERMODYNAMIC MODELING RESULTS

Depth (cm)	pH	Saturation Indexes* $CaCO_3$ ARAGONITE	$CaCO_3$ CALCITE	$CaMg(CO_3)_2$ DOLOMITE	SiO_2 AMORPHOUS	$CaSO_4 \cdot 2H_2O$ GYPSUM	SiO_2 QUARTZ
5	6.9	0.86	1.57	36	0.45	-0.27	0.96
25	6.7	0.63	1.11	20	0.70	-0.10	1.14
45	7.0	1.22	2.23	66	0.61	-0.14	1.09
53	7.1	1.11	2.02	64	0.60	-0.19	1.08
69	7.1	1.25	2.28	56	0.72	-0.04	1.16
79	6.9	0.79	1.44	18	0.74	-0.03	1.17

* SATURATION INDEX = $\frac{\text{Ion Activity Product}}{\text{Solubility Constant}}$. SI > 1, supersaturation, precipitation can occur. SI = 1, saturation, equilibrium. SI < 1, undersaturation, dissolution can occur.

work shows dolomite present at 79 cm but no gypsum. Seawater salinities of above ~125‰ are needed for gypsum precipitation. At the time of sampling, gypsum could only precipitate in the deepest parts of the lake where salinities were much higher (~165‰–170‰). X-ray analyses of a grab sample from the deepest part of the lake indicates the presence of both dolomite and gypsum. Without the active precipitation or occurrence of gypsum in the shallow, matted sediments, it is highly unlikely that the conversion of $CaSO_4 \cdot 2H_2O$ to $CaCO_3$ is a major calcification process as outlined by Friedman and Sanders (1978) for the Dead Sea. In these shallow, matted sediments the continual removal of bacterially produced HCO_3^- leads to the precipitation of $CaCO_3$, which in turn decreases the Ca^{2+} pore-water concentration. This removal of Ca^{2+} as calcium carbonate helps lead to the undersaturation of these fluids with respect to gypsum. This phenomenon appears to be important in hypersaline environments where cyanobacterial mats are present (Lyons et al., 1984). A similar mechanism causing gypsum undersaturation has been proposed for algal mat–rich Laguna Madre sabkha sediments (Amdurer and Land, 1982).

The major question is whether most of this authigenic $CaCO_3$ is produced via evaporitic (i.e., inorganic) or bacterial (i.e., biogenic) processes. The carbon-isotope data of Aharon et al. (1977) indicate that although the calcite in the sediments of Solar Lake is enriched in ^{12}C and is hence produced from HCO_3^- derived from the degradation of the organic carbon, the aragonite is enriched in ^{13}C. These authors have argued that the aragonite found in the sediments precipitated inorganically (by evaporative processes) without incorporation of isotopically lighter HCO_3^- produced through degradation of cyanobacterial mats via sulfate reduction.

If evaporitic precipitation of aragonite was occurring at a relatively rapid rate, this aragonite should be observable in the surficial sediments. Krumbein et al. (1977) have shown by laboratory experiments that aragonite can be precipitated via bacterial processes in the shallow, matted sediments, and they have argued that the aragonite in these sediments is biogenic. These experimental data are supported by their observation that no $CaCO_3$ is observed in the top few centimetres of these shallow, matted sediments and that aragonite increases with depth in these sediments.

The role of evaporitic deposition of $CaCO_3$ in these shallow, matted sediments can be quantitatively evaluated using the technique outlined in Lazar et al. (1983). Using the expression of Lazar et al. (1983), TA and Mg^{2+} data from the seawater just east of Solar Lake in the Gulf of Elat and from the brine just above the surface of the shallow matted sediments, and the limnology of the lake (Eckestein, 1970), we can calculate the amount of evaporitically produced $CaCO_3$. This value is 13 mg $CaCO_3 \cdot cm^{-2} \cdot yr^{-1}$, yielding a deposition rate of $CaCO_3$ throughout the lake of ~ 0.07 mm yr^{-1}. When compared to the total $CaCO_3$ deposition rate of 0.5 mm yr^{-1} (Krumbein et al., 1977), our figure represents only ~15% of the total $CaCO_3$ being deposited. Therefore, we conclude that in the shallow-water, matted sediments of the lake, most of the $CaCO_3$ being produced is due to bacterial degradation processes. This supports conclusions of Krumbein and his co-workers. The discrepancy of the isotope data and these results undoubtedly is due to the fact that the majority of the isotope information is from samples collected in the deeper part of the lake where evaporitic processes are much more influential than bacterial ones. On the basis of the work of Stuermer et al. (1978) and Schidlowski (1983), one might expect that the $\delta^{13}C$ of the $CaCO_3$ in these shallow, matted sediments may be isotopically heavier than the calcite measured by Aharon et al. (1977) because of the heavy value of the original organic matter. These anomalous $\delta^{13}C$ values for cyanobacterial algal-mat organic carbon in Sinai hypersaline lakes have recently been noticed (Matzigkeit and Schidlowski, 1983; Des Marais, 1984). Their relationship to the authigenic carbonate $\delta^{13}C$ values awaits further detailed work.

Interpretation of data for sediment below 25 cm is complicated by the possible dilution of pore water by subterranean influx of less saline brine (Jørgensen and Cohen, 1977). Below 25 cm, the Mg^{2+}/Cl^- ratio decreases and the Ca^{2+}/Cl^- ratio increases. Dolomitization could be controlling these chemical changes. This process is supported by the observation of a minor amount of modern dolomite at ~30 cm in this part of the lake (Aharon et al., 1977) and the results of the thermodynamic modeling, which indicate that the sediments are highly supersaturated with respect to dolomite (Table 1). The dolomite that is found is poorly ordered, appears to be replacing aragonite (the dolomite and replaced aragonite have similar $\delta^{13}C$ signatures), and is forming today (Aharon et al., 1977).

Two mechanisms have been proposed for the cause of dolomite formation. Friedman et al. (1973) suggested that the increase in the Mg^{2+}/Ca^{2+} ratio necessary for the dolomitization reaction is mainly produced by the increase of Mg^{2+} due to the degradation of organic matter and not to Ca^{2+} reduction due to gypsum formation. Aharon et al. (1977) have argued that the dolomite was formed by passing a hot brine with a high Mg^{2+}/Ca^{2+} ratio through the original authigenically deposited aragonite. The high Mg^{2+}/Ca^{2+} ratio is developed from the removal of Ca^{2+} by the precipitation of gypsum. Arguments similar to those proposed by Aharon et al. (1977) have been used for the formation of dolomites in other hypersaline environments, such as Bonaire, Qatar, and Abu Dhabi (Deffeyes et al., 1965; Murray, 1969; deGroot, 1973; McKenzie, 1981; Patterson and Kinsman, 1982).

TABLE 2. REACTIVE SILICATE CONCENTRATIONS AND TITRATION ALKALINITY (TA) FROM SOLAR LAKE PORE FLUIDS

Depth cm	Reactive silicate μmol L^{-1}	Titration alkalinity meq L^{-1}
Overlying	117	2.87
5	494	8.79
25	643	9.09
45	603	8.54
53	610	7.60
69	723	5.89
79	748	5.26

If dolomite is forming in this part of the lake sediments, our results support the mechanism of Friedman et al. (1973). However, more detailed work should be undertaken to establish if, indeed, dolomitization is occurring in these matted sediments at depth, or if these changes in pore-water geochemistry below 25 cm are due to hydrological processes such as mixing with another subsurface brine.

Silicification of stromatolitic structures has been observed frequently in the geologic record (e.g., Poncet, 1981; Awramik et al., 1983). Therefore, the geochemistry of silica in cyanobacterial mats is of geologic interest. Friedman and Foner (1982) observed no loss of weight from 10 g of 1-mm glass beads placed in the mat at Solar Lake over a 9-month period. Yet, our values for pore-water-dissolved reactive silicate (Table 2) substantiate the SEM photos by Krumbein (1978) that depict the dissolution of diatoms in the mats of Solar Lake. Because of the scarcity of detrital silicates in the sediments of Solar Lake (Friedman et al., 1973), these high pore-water values probably result from opaline silica dissolution. This is supported by the fact that the pore waters are undersaturated with respect to amorphous silica (Table 1). Our modeling results indicate that the pore waters of Solar Lake are essentially in equilibrium with respect to quartz (Table 1). Therefore, our results and those of Friedman and Foner (1982) are compatible; that is, biogenic silica is dissolving while quartz is not. Therefore, even though the pH of sediment pore-water ranges from 6.7 to 7.1, $CaCO_3$ is precipitating and opaline silica is dissolving.

CONCLUSIONS

Pore-water data confirm the observations of Krumbein and co-workers (Krumbein et al., 1977; Krumbein and Cohen, 1977; Krumbein, 1978) that the oxidation of the cyanobacterial mat by anaerobic bacteria is a major process leading to the precipitation of $CaCO_3$. In the top 25–30 cm of these mats, Ca^{2+}, Sr^{2+}, and SO_4^{2-} are removed relative to Cl^- in the pore waters. There is no evidence of gypsum precipitation at these depths in the sediments; therefore, SO_4^{2-} is being removed solely by sulfate reduction, and Ca^{2+}, Sr^{2+}, and biologically produced HCO_3^- are being removed as authigenic $CaCO_3$. At depth, it is possible that dolomite or protodolomite is forming at the expense of aragonite as the hot brine sinks through the sediments.

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TI Observations on the ionic composition of blue-green algae growing in saline lagoons
AU Pillai, V. K.
SO Proc. Natl. Inst. Sci. India, (19550000) vol. 21, no. 2, pp. 90-102.

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TI Calcification in cyanobacterial biofilms of alkaline salt lakes.
AU Arp, Gernot (1); Reimer, Andreas; Reitner, Joachim
CS (1) Institut und Museum fuer Geologie und Palaeontologie, Universitaet Goettingen, Goldschmidtstrasse 3, D-37077, Goettingen Germany
SO European Journal of Phycology, (Oct., 1999) Vol. 34, No. 4, pp. 393-403.

Geomicrobiology of carbonate-silicate microbialites from Hawaiian basaltic sea caves
AU Leveille, R. J.; Fyfe, W. S.; Longstaffe, F. J.
CS Department of Earth Sciences, The University of Western Ontario, London, ON, N6A 5B7, Can.
SO Chem. Geol. (2000), 169(3-4), 339-355

Calcification of cyanobacterial mats in Solar Lake, Sinai
TIFR Calcification des mattes cyanobacteriennes dans le Lac Solar, Sinai
AU LYONS W. M. Berry; LONG David T.; HINES Mark E.; GAUDETTE Henri E.; ARMSTRONG Peter B.
CS Univ. N.H., Dep. Earth Sci., Durham, NH, United States
SO Geol. (Boulder), (1984-10), 12(10), 623-626, 2 tabl., 33 refs. Illustrations

Effect of inhibitors on calcium carbonate deposition mediated by freshwater algae
AU Heath, Carolyn R.; Leadbeater, Barry C. S.; Callow, Maureen E.
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SO J. Appl. Phycol. (1995), Volume Date 1995, 7(4), 367-80

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Minireview

Mechanisms of desiccation tolerance in cyanobacteria

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Drying of cells leads to damage resulting from crowding of cytoplasmic components, condensation of the nucleoid, increases in the T_m of membrane phase transitions, and imposition of stress upon cell walls. Prolonged desiccation leads to oxidation of proteins, DNA and membrane components through metal-dependent Fenton reactions, while Maillard reactions generate cross-linked products between the carbonyl groups of reducing sugars and the primary amines of nucleic acids and proteins. Although such damage restricts many organisms to aqueous environments, some, including many cyanobacteria, can tolerate the air-dried state for prolonged periods. Cyanobacteria in the Tintenstrich communities of exposed rock faces, *Microcoleus* and *Lyngbya* spp. in intertidal mats, chasmoendolithic *Chroococcidiopsis* spp. in the rocks of hot and cold deserts, and terrestrial epilithic crusts of *Tolypothrix* and *Nostoc* are examples that show a marked capacity to withstand the removal of their cellular water. For *Nostoc commune*, the mechanisms of desiccation tolerance reflect both simple and complex interactions at the structural, physiological and molecular levels.

Key words: cyanobacteria, desiccation, nucleic acids, membranes, EPS, *Nostoc*

Introduction

The mechanisms of desiccation tolerance are not well understood despite the fact that numerous prokaryotic and eukaryotic organisms are capable of surviving more or less complete dehydration, and the current intense interest in long-term storage and survival of cells (Kennedy *et al.*, 1994; Oliver *et al.*, 1998; Billi & Potts, 1999). Available evidence suggests that desiccation tolerance reflects the sum of numerous simple and complex interactions at the structural, physiological and molecular levels. For example, the effects of reactive oxygen species in desiccation damage are exacerbated by high light and UV irradiation (Garcia-Pichel & Castenholz, 1999). As a consequence, desiccation is of particular significance for plants, algae (including intertidal forms and those in lichen associations) and cyanobacteria that generate oxygen during photosynthesis. The mechanisms used by photosynthetic organisms to withstand water deficit are therefore of considerable interest. One cyanobacterium, *Nostoc commune* Vaucher, is the focus of studies to understand desiccation tolerance at the molecular level (Potts, 1994, 1999). In this brief account, desiccation is considered from the perspective of: (1) changes to cell macromolecules, (2) mechanisms that contribute to desiccation tolerance, and (3) the significance of these mechanisms in cyanobacteria. Many of the biophysical considerations presented here are taken from Potts (1994).

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Cyanobacterial populations subject to desiccation

Cyanobacteria dominate the bacterial populations of many extreme environments (Whitton & Potts, 1999) such as deserts (Palmer & Friedmann, 1990; de Chazal *et al.*, 1992), thermal springs (Ward *et al.*, 1989), hot brines (Dor & Paz, 1989), frigid lakes (Orcutt *et al.*, 1986), soda lakes (Ciferri, 1983) and the nutrient-poor open ocean (Fogg, 1982). Cyanobacteria that experience extremes of desiccation, include intertidal marine mats, often dominated by a form species of *Microcoleus* (Pentecost, 1985; Potts, 1977; Potts & Whitton, 1977, 1980), growths of *Gloeocapsa* in Tintenstrich communities, and terrestrial crusts of *Tolypothrix*, *Calothrix* and *Nostoc* (Whitton *et al.*, 1979; Potts & Whitton, 1980; Whitton, 1992; Amarpalli *et al.*, 1997; Tripathi *et al.*, 1997). Some cyanobacteria, and also eukaryotic algae, are sufficiently desiccation-tolerant to survive long-distance transport in aerosols over Antarctica (Marshall & Chalmers, 1997). Many of these communities also include forms that resist the effects of high doses of ionizing radiation (Table 1).

One aspect of the ecophysiology, biochemistry and molecular biology of cyanobacteria which deserves attention with regard to desiccation tolerance is the synthesis, identity and function of extracellular polysaccharides (Philippis & Vincenzini, 1998; Adhikary, 1998). These biopolymers regulate the loss and uptake of water from cells, serve as a matrix for the immobilization of other components of the cell which may offer protection (e.g. UV-absorbing compounds) and may protect cell walls

Calcification in cyanobacterial biofilms of alkaline salt lakes

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Geomicrobiological analysis of calcifying biofilms of three alkaline salt lakes characterized by moderate to high carbonate alkalinity indicates that microbial carbonate rock formation is not directly linked to cyanobacterial carbon fixation. The present review summarizes results from two published case studies that have been carried out at Pyramid Lake, USA, and Lake Nuoertu, PR China. New observations and data are presented for a current project on Satonda Crater Lake, Indonesia, that revise previous conclusions concerning the relationship between cyanobacteria and biofilm calcification. Extracellular polymeric substances (EPS) in the investigated lakes are mostly produced by cyanobacteria; their properties are discussed as key factors in biofilm calcification. In particular, EPS are capable of binding divalent cations (e.g. Ca^{2+}) from the liquid phase by their carboxylate and sulphate groups. Therefore, despite a high supersaturation of the lake water with respect to calcium carbonate minerals, precipitation does not take place immediately. A delayed onset of precipitation can be achieved by a continuous Ca^{2+} supply that exceeds the Ca^{2+}-binding capacity of the EPS, and/or an exoenzymatic degradation (decarboxylation, cleavage) of mucous substances that reduces the binding capacity and causes secondary Ca^{2+} release. The resulting microcrystalline precipitates are randomly distributed within the EPS, usually away from any of the living cyanobacteria. This suggests that the effect of photosynthetic CO_2 fixation in increasing supersaturation is of secondary importance at high alkalinities. In contrast to biofilm-covered surfaces, calcium carbonate minerals nucleate and grow rapidly at surfaces poor in EPS when the critical supersaturation level for non-enzymatically controlled carbonate precipitation is reached. Examples of such surfaces poor in EPS are dead, lysed green algal cells and thin, discontinuous biofilms in voids of microbial reef rocks. Calcium carbonate crystals directly linked to cyanobacterial cells or filaments have been observed only exceptionally, e.g. on *Calothrix*.

Key words: biofilm, calcification, cyanobacteria, exopolymers, soda lakes, stromatolites

Geological significance of calcifying cyanobacterial biofilms and stromatolites

Traditionally, ancient laminated reef-like carbonates, commonly called stromatolites (Kalkowsky, 1908), have been attributed to $CaCO_3$ deposition linked to cyanobacteria or cyanobacterial mats (Monty, 1977). Trapping and binding of carbonate particles and mud have been considered as the main mechanisms in their formation, stimulated by the discovery in the late 1960s of marine agglutinated stromatolites (Shark Bay, Bahamas) (Black, 1933; Logan, 1961). Today, *in situ* precipitation of carbonate minerals within microbial mats is recognized to be of crucial importance in the formation of these structures. In addition to mineralizing cyanobacteria-dominated mats, examples of non-cyanobacterial and even non-phototrophic communities are known to produce stromatolites (e.g. Keupp & Arp, 1990; Böhm & Brachert, 1993).

The oldest known stromatolites (Archean) are difficult to interpret and were probably formed by non-cyanobacterial communities (Walter, 1994). In the absence of positive evidence and fractal analysis of morphological characteristics some of these Archean stromatolites may not necessarily be linked to biological activity (Grotzinger & Rothman, 1996). During Middle and Upper Proterozoic times stromatolites reached their peak in abundance and distribution, even forming carbonate platforms comparable in size to Recent reef platforms (Awramik, 1971; Walter & Heys, 1985; Grotzinger, 1994). It is still an enigma as to why stromatolites vanished to a great extent during the late Precambrian and why they re-occurred sporadically in later periods. Consensus exists only with regard to the relationship between the flourishing of calcareous marine plankton and the lack of marine stromatolites since the late Mesozoic. Since cyanobacteria-associated calcification and stromatolite formation are dependent on environmental prerequisites, several hypotheses have been developed that argue for changes in the Ancient ocean chemistry (Riding, 1982; Kempe & Degens, 1985; Grotzinger, 1990; Knoll *et al.*, 1993; Kempe & Kazmierczak, 1994).

Suggestions with regard to the chemical composition of the ocean waters during the course of the Precambrian vary considerably and remain hypothetical. There is evidence that the composition of even the Phanerozoic oceans oscillated considerably over geological time (Hardie, 1996). Only a few examples are given here, without discussing the validity of assumptions and analysis. For the Precambrian, Knauth (1998) recently proposed that the salinity of the early ocean might have

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been 1.5 to 2 times that of the modern value. In contrast earlier assumptions (e.g. Holland, 1992) were of salinities comparable to that of the modern ocean. In a far-reaching hypothesis, Kempe & Degens (1985), later extended by Kempe & Kazmierczak (1994), argued for the evolution of an early highly alkaline ocean ('soda ocean hypothesis'), based on geochemical, mass balance and kinetic considerations and on observations on sodium carbonate-rich salt lakes (soda lakes). The establishment of an ocean (4.5 to 1 billion years before present) with pH values of 9 to more than 10 is critically dependent on low atmospheric pCO_2 values comparable to the modern level of $10^{-3.5}$ atm. This is in contrast to most current views and models that argue for high pCO_2 atmospheric conditions to account for a greenhouse effect that kept the early Earth from freezing (e.g. Kasting, 1987, 1992; Holland & Kasting, 1992). On the basis of mineral associations in palaeosoils, Holland (1994) proposed that the pCO_2 was $\leqslant 10^{-2.0}$ atm between 2.75 and 2.2 billion years ago (late Archean and early Proterozoic). Consequently, lower, near-neutral or slightly acidic pH values are to be expected for the ocean under such conditions. However, the recent discovery of Archean glacial sediments as old as 2.9 billion years suggest that a significant drawdown of the atmospheric pCO_2 might have occurred earlier than previously suggested (Young *et al.*, 1998). From this point of view one may regard various alkaline salt lakes as 'model Precambrian oceans', which could reveal the principal processes of precipitation in cyanobacteria-dominated biofilms and mats, and contribute to a better understanding of ancient ocean chemistry. This review article summarizes results from two case studies on highly alkaline salt lakes that were carried out in the USA (Pyramid Lake; Arp *et al.*, 1999) and PR China (Lake Nuoertu; Arp *et al.*, 1998). A preliminary report on microbial communities of the moderately alkaline, marine Satonda Crater Lake, Indonesia, was given by Arp *et al.* (1996).

Alkaline salt lakes of a high carbonate alkalinity are characterized by low to very low Ca^{2+} concentrations (5 mmol l^{-1} to less than 0.1 mmol l^{-1}) compared with seawater (10 mmol l^{-1}). As sodium is partly balanced by carbonate alkalinity (sum of charges of HCO_3^- and CO_3^{2-} ions) these lakes are commonly called 'soda lakes'. It is important to note that $CaCO_3$ supersaturation in these lakes is achieved even at a very low Ca^{2+} concentration, because the ion activity product necessary to start precipitation is exceeded by high carbonate concentrations. In other words, the solubility product implies that high $HCO_3^- + CO_3^{2-}$ concentrations are coupled with very low to only trace amounts of Ca^{2+} (see for example Eugster & Hardie, 1978). Despite low Ca^{2+} concentration in the water column a large amount of $CaCO_3$ can be formed within a geologically short time if the Ca^{2+} supply rate is high enough. Consequently, $CaCO_3$ deposits of alkaline salt lakes are either linked to local Ca^{2+} influx (thermal/artesian springs) or physicochemical fluctuations of the whole lake (fluctuating ratio of evaporation/influx).

For kinetic reasons (complexing, seed crystal poisoning) a non-enzymatically controlled precipitation of $CaCO_3$ minerals is only observed in natural waters and laboratory experiments after an appropriate supersaturation is exceeded (e.g. Kempe & Kazmierczak, 1990*b*; Svensson, 1992). Empirical values of supersaturations (9-fold for calcite and 8-fold for aragonite) are the basis for hydrochemical model calculations discussed in the case studies below.

Processes involved in biofilm calcification

In general, $CaCO_3$ precipitation in cyanobacterial mats and biofilms is promoted by at least the following two processes: (1) A shift of the carbonate equilibrium (microgradient) by the physiological activity of microorganisms, and (2) the provision of sites for heterogeneous nucleation. The simplified, overall reaction of $CaCO_3$ precipitation by photosynthetic CO_2 removal (for review of carbon dioxide and bicarbonate assimilation see Raven, 1970), is (Kelts & Hsü, 1978; Usdowski *et al.*, 1979):

$$Ca^{2+} + 2\,HCO_3^- \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Nucleation occurs, for example, at or within the sheaths of cyanobacteria (Pentecost & Riding, 1986). Further processes that can enhance $CaCO_3$ mineral supersaturation are linked to non-phototrophic members of biofilms and microbial mats (for review see e.g. Krumbein, 1979). In principle, the effect of CO_2 fixation on the carbonate equilibrium by chemolithotrophs is identical to that of photosynthesis except that the organisms obtain energy from inorganic electron donors.

Bacterial sulphate reduction can be significantly involved in alkalinity production in sulphate-rich environments. The process can be summarized by the following model reaction (Kempe, 1990), whereby organic matter is given in a Redfield ratio:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53\,SO_4^{2-} + 14H_2O \rightarrow$$
$$106\,HCO_3^- + 16\,NH_4^+ + HPO_4^{2-} 53\,HS^- + 14\,OH^-$$

Further, anaerobic methane oxidation coupled with sulphate reduction produces alkalinity and has been suggested as a driving mechanism for the precipitation of carbonate cements at marine, methane-supplying seeps (equations and further discussion in Paull *et al.*, 1992). Excess alkalinity results from the reaction of ferrous iron and sulphide to form pyrite:

$$SO_4^{2-} + CH_4 \rightarrow HCO_3^- + HS^- + H_2O$$

Degradation of organic compounds via nitrate reduction and ammonification produces alkalinity and ammonia by the following model reaction (Kelts, 1988):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\,NO_3^- \rightarrow 7.2\,CO_2 +$$
$$98.8\,HCO_3^- + 16\,NH_4^+ + 42.4\,N_2 + HPO_4^{2-} + 49\,H_2O$$

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acids ammonia is also produced (Kelts & Hsü, 1978), as described by:

$$CH_2NH_2COOH + 2\,(H) \rightarrow NH_3 + CH_4 + CO_2$$
$$NH_3 + CO_2 + H_2O \rightarrow NH_4^+ + HCO_3^-$$
$$NH_3 + HCO_3^- \rightarrow NH_4^+ + CO_3^{2-}$$

Methanotrophy and nitrate reduction (ammonification) principally occur in microbial mats, but their significance is difficult to estimate, except that sources of methane (e.g. seeps) or oxidized nitrogen compounds (e.g. following mineralization and nitrification of proteinous material) are obvious.

Properties and effects of acidic exopolymers

Extracellular polymeric substances (EPS) are of crucial importance for the initial attachment of micro-organisms to substratum surfaces, and for the development of biofilms and microbial mats (for reviews see Decho, 1990; Brading *et al.*, 1995; Little *et al.*, 1997). These highly hydrated polymers permit the establishment of protective microhabitats by decreasing diffusion rates, and buffer sudden ionic and environmental changes of the surrounding macroenvironment.

Under natural conditions EPS are known to consist to a great extent of acidic macromolecules, mainly carboxylated polysaccharides (uronic acids) (Decho, 1990; Trichet & Defarge, 1995; Fortin *et al.*, 1997). Sulphate, phosphate and hydroxyl groups contribute to a varying but generally lower extent to the acidic property. From laboratory studies it is known that uronic acids of bacterial EPS increase under stress conditions (Uhlinger & White, 1983). This response corresponds to suboptimal growth conditions common in nature. Because of their reactive acidic groups, biofilm EPS sequester dissolved organic matter (DOM), nutrients and metals from the liquid phase (Decho, 1990; Ferris, 1993). Complexing of metals, above all heavy metals, at the EPS of biofilms has been extensively studied with regard to sewage treatment plants. Magnesium, calcium and – depending on their redox state – iron, manganese and other heavy metals are bound to carboxyl groups, and are removed from the liquid phase by means of an equilibrium reaction. Therefore, EPS react as a kind of 'ion exchange resin'.

Diffusion of ions is thereby maintained until binding capacity is reached. Due to the pH-dependent deprotonation of carboxyl groups, metal binding increases with pH (Ferris *et al.*, 1989). It should be noted that the deprotonation should lower the pH near the acidic groups at least for a short time before bulk phase buffering eliminates the effect. The lowering of pH is also more than compensated by the CO_2 assimilation of the phototrophs since only a maximal one carboxyl group is formed per hexose monomer and six moles of CO_2 are assimilated to produce one mole of hexose.

In contrast to enzymatically controlled biomineralization (Addadi & Weiner, 1989; Mann, 1989), acidic macromolecules and their side groups are stereochemically highly disordered in biofilms. Consequently, temporally retarded precipitation may only start at suitably arranged acidic groups. From this point of view, the co-occurrence of calcified and non-calcified cyanobacteria as well as the co-occurrence of microcrystalline and microsparitic precipitates might reflect differences in the biochemical composition of EPS with regard to the number of acidic groups and their stereochemical arrangement.

Material and methods

For sampling procedures, fixation, embedding, hard-part microtomy and water chemistry analysis of the material presented here see Arp *et al.* (1998). Epifluorescence images were obtained using a Zeiss Axioplan microscope equipped with a Peltier-cooled VISICAM-colour CCD-camera (PCO Computer Optics, Kehlheim, Germany). Image stacks with a Z-spacing of 0.5 or 0.25 μm were obtained by using a piezo-mover (Physik Instrumente, Waldbronn, Germany) attached to a 'Plan-Apochromat' ×63 objective (Zeiss, NA = 1.4). Image processing and three-dimensional restoration were carried out using Metamorph Imaging software (Universal Imaging, West Chester, PA) and EPR deconvolution software (Scanalytics, Billerica, MA).

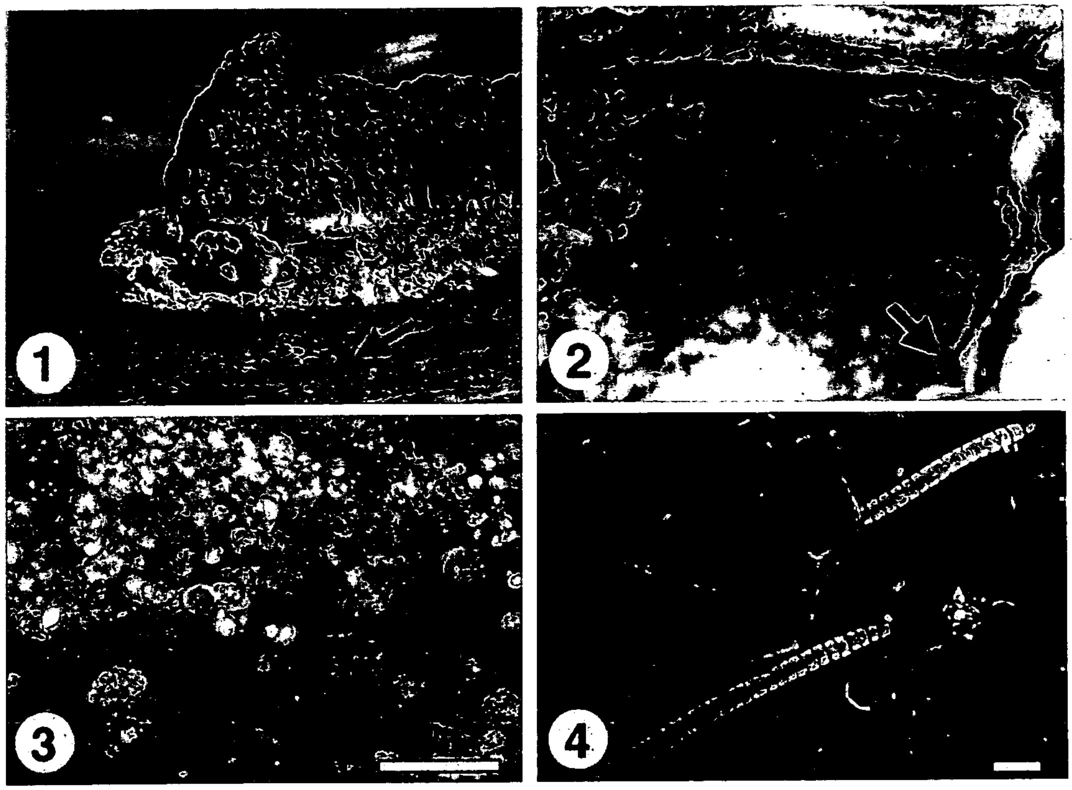
Parameters of the carbonate system, partial pressure of CO_2 (pCO_2) and the saturation with respect to calcite and aragonite, were calculated with the program PHREEQE (Parkhurst *et al.*, 1990). Saturation is given by the saturation index, $SI = \log\ (IAP/K_{SO})$ (Stumm, 1992), where IAP denotes the ion activity product and K_{SO} is the solubility product of the corresponding mineral (solid phase).

Results

Calcifying biofilms at thermal springs, Pyramid Lake

Pyramid Lake is a large, deep, hyposaline lake 50 km northeast of Reno (Galat & Jacobsen, 1985). The lake water is highly supersaturated with respect to $CaCO_3$ minerals ($SI_{Cc} = 1.19$, $SI_{Ar} = 1.04$; Table 1) with a pH of 9.3 and an alkalinity in the range of 20 meq L^{-1} (Galat & Jacobsen, 1985; Arp *et al.*, 1999). During the Pleistocene, calcareous ikaite pinnacles up to 100 m high ('The Needle Rocks', Fig. 1) formed at the northeastern shore, when thermal springs of a NNE–SSW trending fault system discharged into the cold, deep lake (Benson, 1994). Today, only relictual thermal springs and seepage sites are active at the base of the pinnacles. In addition, two wells were drilled that eject hot water.

Ca^{2+}-supplying (5.5 mmol l^{-1}) thermal water flowing off one of the wells mixes with alkaline lake water (22.08 mequiv l^{-1}, pH 9.3), finally resulting in microcrystalline carbonate precipitates suspended in the water column ('whiting'; cf. Bathurst, 1975, p. 137) of the affected bay



Figs 1–4. Calcifying cyanobacterial biofilms of thermal littoral pools at Pyramid Lake, Nevada. Fig. 1. Field view of 'The Needle Rocks' on the northwest shore of the lake. Hot water being ejected from a well (arrow on right) mixes with alkaline lake water causing a 'whiting' (suspended microcrystalline $CaCO_3$) in an embayment. The investigated pool of mixed thermal and lake water is located between large tufa boulders at the base of a Pleistocene pinnacle (arrow to left). The car at the right margin of the image gives the scale. Fig. 2. Detail of the investigated pool. The rim is veneered by calcifying cyanobacteria-dominated biofilms that display a colour zonation. Submerged parts show pale to brownish biofilms. At the water level a green zone (dark in the photograph), with a reddish underlayer of purple bacteria, grades into a paler yellowish splash zone above. The arrow points to the inflow of 64 °C water from a fissure. The photograph covers an area approximately 50 cm wide. Fig. 3. Hard-part section of a brownish biofilm at 10 cm depth (43 °C). $CaCO_3$ precipitates in the biofilm are concentrated within a distinct zone near the interface with the liquid phase (upper part of the image). The biofilm is largely produced by a cyanobacterial species of the LPP group ('*Oscillatoria*'). Nomarski optics. Scale bar represents 50 μm. Fig. 4. Epifluorescence micrograph of a Calcein-contrasted hard-part section of the same sample, shown in Fig. 3. Microspar crystals are scattered within the highly hydrated EPS, not apparently associated with the filamentous cyanobacteria ('*Oscillatoria*'), and coccoid phototrophs. Scale bar represents 10 μm.

(Fig. 1) (Arp *et al.*, 1999). Physicochemical calculation of mixing these waters results in a pH of 8.8 and a theoretical 65-fold supersaturation ($SI_{Ar} = 1.81$) with regard to aragonite. Given an aragonite precipitation at 8-fold supersaturation ($SI_{Ar} = 0.9$), the pH is decreased to 8.1. Calculated pH and alkalinity (6.94 mequiv l^{-1}) closely correspond to field measurements in the bay (pH 8.08; alkalinity 7.67 mequiv l^{-1}). Consequently, the observed precipitation can be regarded as physicochemically driven. A similar situation to the whiting-affected bay is found in a thermal pool between tufa boulders of the pinnacles (Figs 1, 2). Ca^{2+}-supplying thermal water coming out of a fissure mixes with alkaline lake water that spills into the pool via two narrow connections. In contrast to the bay, pool waters remain clear, but the cyanobacteria-dominated biofilms at its rim are impregnated by $CaCO_3$ precipitates. Thin sections of the *Oscillatoria*- and *Phormidium*-dominated biofilms show that precipitation is spatially concentrated within the EPS where it contacts the liquid phase (Fig. 3). The microcrystalline to microsparitic aragonite crystals nucleate in a randomly distributed way within the highly hydrated mucous substances of the biofilm margin. The immediate surroundings of cyanobacterial filaments and coccoid phototrophs remain uncalcified (Fig. 4).

Table 1 models the mixing of Ca^{2+}-containing thermal spring water and alkaline lake water analogous to the situation described above. Theoretically a 55-fold supersaturation ($SI_{Ar} = 1.74$) with regard to aragonite is calculated for the 46.5 °C waters of the thermal pool. This temperature corresponds to that of the site where the cyanobacterial biofilms illustrated in Figs 3 and 4 were sampled. Adjusted to an aragonite precipitation value ($SI_{Ar} = 0.9$) and to pCO_2 in equilibrium with the atmosphere, a pH of 8.95 and an alkalinity of 5.75 mequiv

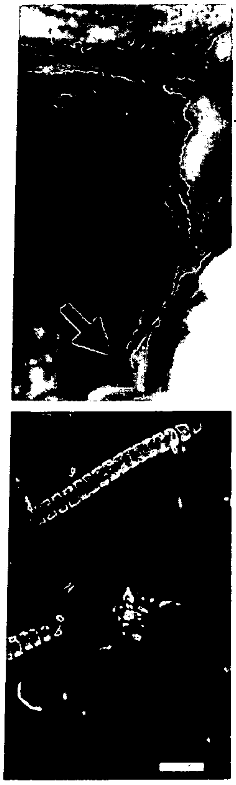


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Table 1. Representative water chemistry data of spring and lake water of Pyramid Lake (USA), Lake Nuoertu (PR China) and Satonda Crater Lake (Indonesia)

Sample	Temp. (°C)	pH	EC (mS cm^{-1})	E_h (mV)	O_2 (mmol l^{-1})	Tot Alk (mequiv l^{-1})	Ca (mmol l^{-1})	Mg (mmol l^{-1})	SI_{Ar}	SI_{Cc}	pCO_2 (μatm)
Pyramid Lake, The Needle Rocks											
(sampling period May 1996)											
Lake water (surface)	15·8	9·30	7·27	390	0·254	22·08	0·26	3·29	1·04	1·19	333
Thermal spring at Needle Rocks	65·5	7·14	5·97	102	0·063	1·96	3·99	1·23	0·04	0·15	13 760
Thermal pool, calculated (60% lake water, 40% spring water)	46·5	8·72				8·58	2·50	2·05	1·74	1·87	1007
Thermal pool, calculated (60% lake water, 40% spring water) SI_{Ar} is set at 0·9 pCO_2 is set at 330 μatm	46·5	8·9				5·75	0·37	2·05	0·90	1·03	330
Lake Nuoertu											
(sampling period September 1994)											
Lake water (surface)	17·8	10·0	91·2		0·150	624·3	0·073	6·15	0·96	1·11	318
Spring water	18·2	8·1	0·68		0·209	1·55	0·705	0·740	−0·16	−0·01	626
Mixing zone water, calculated (50% lake water, 50% spring water)	18·0	10·1				297·1	0·459	3·28	1·71	1·86	97
Mixing zone water, calculated (50% lake water, 50% spring water) SI_{Ar} is set at 0·9 pCO_2 is set at 330 μatm	18·0	9·81				296·3	0·746	3·28	0·90	1·05	330
Satonda Crater Lake											
(sampling period October 1993)											
Lake water, 0·1 m depth	30·7	8·58	38·9	272	0·224	4·17	6·64	42·5	0·84	0·98	275
(sampling period June 1996)											
Lake water, 0·1 m depth	30·6	8·50	37·8	274	0·224	3·97					

From Arp *et al.* (1998, in press and unpublished data).
Mixing zone waters are discussed in the text. The water chemistry analysis of Lake Nuoertu (see Arp *et al.*, 1998) has been corrected for calcium. EC, electrical conductivity. Saturation index (SI) is given on a logarithmic scale, which means saturation is reached at SI = 0, and SI = 1 denotes a 10-fold supersaturation (Ω). Ar, aragonite; Cc, calcite.

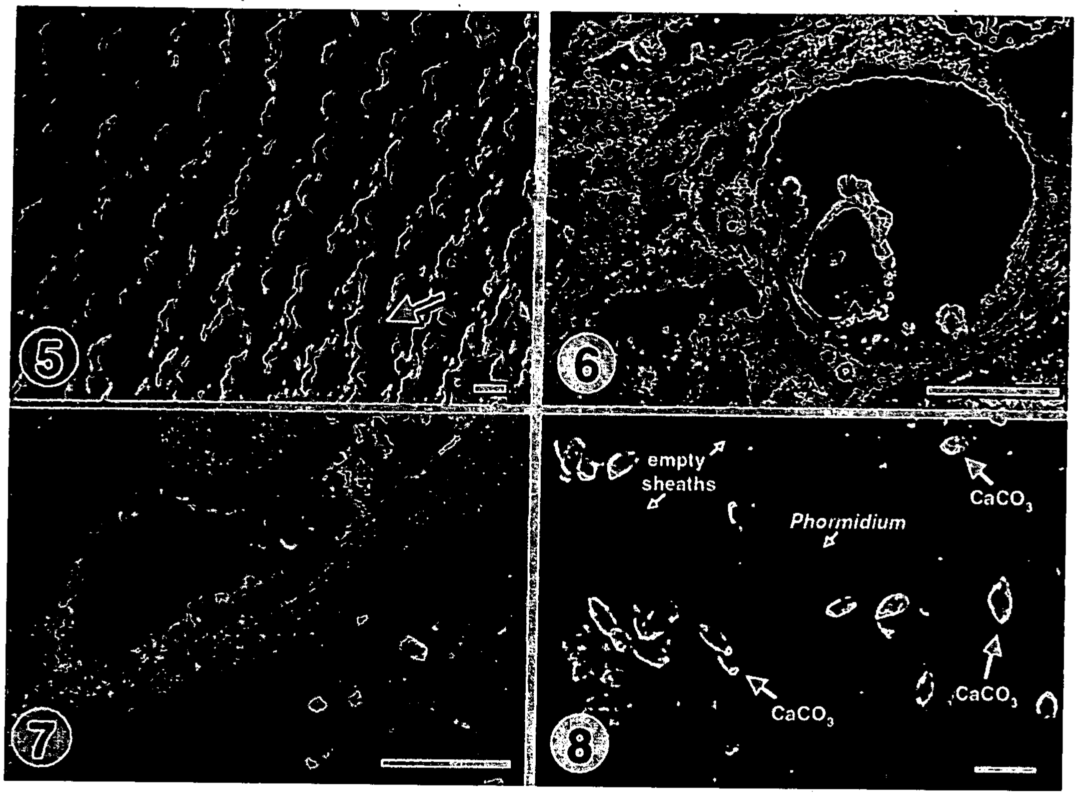
l^{-1} are calculated. The measured pH of 8.7 at the sampling site is slightly lower than the calculated value, indicating that the pCO_2 at this site is slightly higher and not fully in equilibrium with the atmosphere.

On the basis of the concept of EPS-mediated precipitation it is concluded that biofilm calcification within this highly supersaturated, alkaline pool is controlled by the diffusive Ca^{2+} supply, which exceeds the Ca^{2+}-binding capacity of the outermost mucus parts. Photosynthetic CO_2 removal apparently has no significant effect on the precipitation. Biomarker analysis of a living cyanobacterial biofilm, its subfossil stromatolitic crust and a Pleistocene stromatolite indicate that the nature of the cyanobacterial communities does not appear to be critical for the formation of stromatolitic crusts in Pyramid Lake (Arp *et al.*, 1999).

Calcifying biofilms of spring mounds, Lake Nuoertu

Lake Nuoertu is a highly alkaline, hypersaline lake located in the Badain Jaran Sand Sea of Inner Mongolia, PR China (Hofmann, 1996; Arp *et al.*, 1998). It is one of several salt lakes of varying chemistry situated between sand dunes 200–300 m high (Fig. 5). Lake Nuoertu is highly alkaline (624.5 mequiv l^{-1}) with a pH of 10 and a supersaturation of $SI_{Cc} = 1.11$ and $SI_{Ar} = 0.96$. Inflow is assumed to be almost exclusively from groundwater because rain precipitation does not exceed 113 mm per year in this area. Reef-like carbonate pinnacles form at sublacustrine, Ca^{2+}-supplying springs (Arp *et al.*, 1998). Analogous structures, 'spring mounds' or 'tufa pinnacles', are known from a number of Recent alkaline salt lakes (Russel, 1889; Scholl, 1960; Scholl & Taft, 1964; Kempe *et al.*, 1991; Council & Bennett, 1993; Benson, 1994), but have also been described from Tertiary lakes (Hollaus, 1969; Arp, 1995). A characteristic feature of these mounds is porous limestones that show lenticular voids ('sickle-cell limestones') and gas bubbles (Reis, 1926; Arp, 1995). The formation of thin carbonate laminae bridging over lenticular voids remained puzzling in early investigations (e.g. Reis, 1926).

As in the previous case study from Pyramid Lake, physicochemical calculation of mixing equal parts of spring and lake waters shows an extreme theoretical supersaturation (51-fold supersaturation; $SI_{Ar} = 1.71$) with regard to aragonite and a pH of 10.1 (Table 1). Equilibrated to an aragonite saturation index of 0.9 and atmospheric pCO_2, a pH of 9.81 and an alkalinity of 296.3 mequiv l^{-1} are to be expected. Unfortunately, no field data from the mixing zone are available to test the validity of the modelling. However, the theoretical calculations

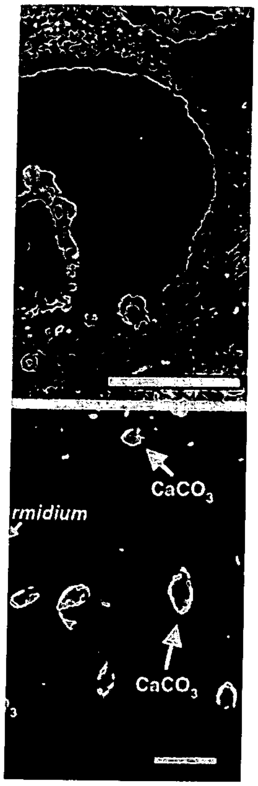


Figs 5–8. Calcifying cyanobacterial biofilms of spring mounds at Lake Nuoertu, Badain Jaran Desert, PR China. Fig. 5. LANDSAT image showing numerous salt lakes located between SSW–NNE trending megadunes of the southern Badain Jaran Desert. Lake Nuoertu is indicated by an arrow. Scale bar represents 2 km. Fig. 6. Mucilaginous biofilm of the spring mound surface at the water line, showing initial aragonite precipitates and their spatial concentration around shrinkage voids and a gas bubble. Cross-polarized light. Scale bar represents 1 mm. From Arp *et al.* (1998) with permission of SEPM. Fig. 7. Microcrystalline laminae form at the border of shrinkage voids within the mucilaginous biofilm by spatial concentration and further growth of the initially precipitated aragonite crystals. Note the increased birefringence of successively cleaved polysaccharides in partly dehydrated areas (arrows). Epitaxial 'inorganic' precipitation of acicular to botryoidal aragonite is restricted to EPS-poor surfaces within water-filled voids. Cross-polarized light. Scale bar represents 1 mm. From Arp *et al.* (1998) with permission of SEPM. Fig. 8. Epifluorescence micrograph of initial aragonite precipitates ($CaCO_3$) within the mucilaginous matrix of a *Phormidium* biofilm. In this partly altered mucus (undergoing decomposition by bacterial exoenzymatic cleavage) only a few living cyanobacterial filaments are left. Excitation 450–490 nm, emission 520–575 nm. Scale bar represents 10 μm.

suggest that $CaCO_3$ precipitation and calcification of biofilms are primarily driven physicochemically.

Shallow parts of the mounds are covered by cyanobacteria-dominated biofilms showing several *Phormidium* morphotypes and less abundant *Spirulina* and coccoid cyanobacteria (*'Aphanocapsa'*). Spring mound samples taken between 45 cm water depth and the surface show the development of sickle-cell structures. These structures originate from successive mineralization of mucilaginous *Phormidium* biofilms during their degradation (Figs 6, 7). Initial precipitates are scattered micrometre-sized aragonite crystals within the EPS without any particular spatial relationship to the cyanobacteria (Fig. 8). At less than 30 cm depth, biofilms are affected by shrinkage processes leading to lenticular voids and gas bubble formation (Figs 6, 7). The occurrence of shrinkage voids and bubbles coincides with an increase in size and abundance of crystals towards marginal parts of the EPS. Viewed under crossed polarized light, an increasing birefringence of the EPS is observed towards the mineralizing biofilm margins (Fig. 7). This increased birefringence indicates an alteration of the mucous substances and has been considered to reflect an increased ordering of polymers. In addition, the shrinkage of the mucus causes a spatial concentration of initial precipitates. Carbonate crystal aggregates, placed in direct contact with liquid-filled voids, serve as nucleation sites for aragonite needle cements and botryoids (Figs 6, 7).

Exoenzymatic cleavage and decarboxylation by the numerous bacteria present should lead to shorter, less branched polysaccharides (increasingly ordered), a loss of hydration, and a loss of functional groups (Arp *et al.*, 1998). The last process implies a decrease in Ca^{2+}-binding capacity. Release of Ca^{2+} from cyanobacterial exopolymers by enzymatic degradation has also been considered to promote calcification of gastropod faecal pellets



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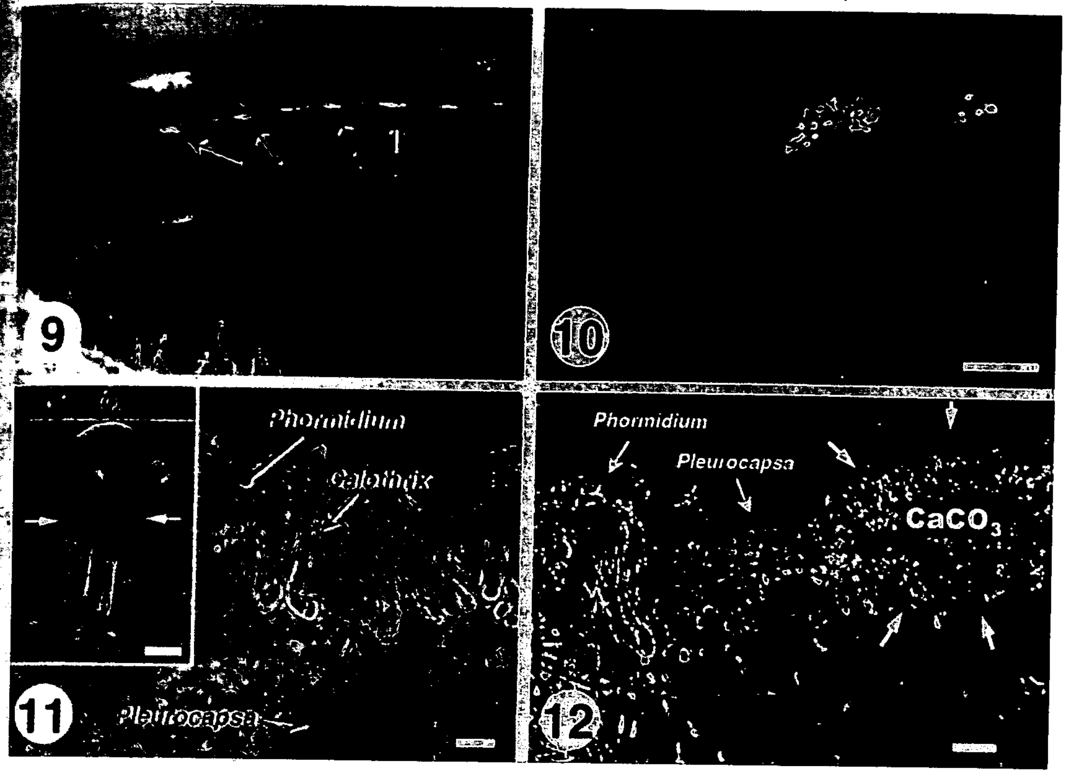

Figs 9–12. Calcification in cyanobacterial biofilms of red algal–microbial reefs of Satonda Crater Lake, Indonesia. Fig. 9. Field view of the lake during the dry season in October 1993. The margin of the lake shows exposed tops of the reefs with white patches of protruding shore sections (arrows). Today there is no contact with the surrounding seawater (background). Fig. 10. Hemispherical cells of a unicellular cyanobacterium ('*Dermocarpella*') on the surface of calcareous red algal reefs. Collected in the dry season (October) 1993, 5 m depth. Epifluorescence micrograph, excitation 450–490 nm, emission 520–575 nm. Scale bar represents 10 μm. Fig. 11. Vertical section of a reef-top biofilm showing *Calothrix* filaments within a plexus of *Phormidium*. The coccoid *Pleurocapsa* occurs preferentially near the hard substratum. Collected at 0.3 m depth, wet season (June) 1996. Phase contrast. Scale bar represents 25 μm. Inset: A barrel-shaped carbonate crystal enclosing the middle parts of a *Calothrix* trichome and a corresponding optical XZ section (arrows) across the semitubular crystal. Collected at 0.9 m depth, wet season (June) 1996. Epifluorescence micrograph, excitation 450–490 nm, emission 520–575 nm. Scale bar represents 10 μm. Fig. 12. Microcrystalline carbonate aggregate at the top of a *Phormidium–Calothrix–Pleurocapsa* biofilm. Note that living cyanobacteria (*Phormidium, Pleurocapsa*) remain free of precipitates, whereas the carbonate (area marked by arrows) nucleates within the EPS in no particular relationship to them. Collected at 0.6 m depth. Overlay of an epifluorescence and crossed nicols image, excitation 450–490 nm, emission 520–575 nm. Scale bar represents 25 μm.

by Trichet & Défarge (1995, p. 207). Together with the diffusive Ca^{2+} supply from liquid-filled voids the Ca^{2+}-binding capacity should be preferentially exceeded in altered, marginal mucus. At places of direct carbonate–water contact, precipitation occurs without the inhibitory effect of EPS. Again, there is no indication that cyanobacteria actively trigger $CaCO_3$ precipitation in this high-alkalinity setting.

Calcifying biofilms of red algal–microbial reefs, Satonda Crater Lake

Lake Satonda occupies the caldera of a small volcanic island North of Sumbawa, Indonesia (Fig. 9) (Kempe & Kazmierczak, 1990*a*, *b*, 1993; Kempe *et al.*, 1997). The lake is filled with altered sea water that is now divided by chemical stratification into two anoxic bottom layers and a seasonally mixed, oxic surface layer. Mixolimnion waters are characterized by a pH of 8.3–8.6, Ca^{2+} concentrations (4.6–5.6 mmol l^{-1}) that are moderately low in comparison with seawater (10 mmol l^{-1}), and an alkalinity of 3.7–4.2 mequiv l^{-1} (Kempe & Kazmierczak, 1990*a*, *b*, 1993; Kempe *et al.*, 1997). The raised alkalinity in the mixolimnion results from seasonal mixing of the uppermost parts of the anoxic, sulphate-reducing bottom waters. Basic water chemistry data of surface waters from the dry season (October 1993) and the end of the wet season (June 1996) are listed in Table 1. Supersaturation with respect to calcium carbonate minerals ($SI_{Calcite} \approx 0.9$; $SI_{Aragonite} \approx 0.8$) exceeds values that are empirically necessary for non-enzymatically controlled precipitation (Kempe & Kazmierczak, 1990*b*).

The lake is of special interest because it provides the physicochemical conditions favourable for stromatolite

formation within a marine setting, as suggested by geochemical models of the ancient ocean chemistry of Kempe & Degens (1985) and Kempe & Kazmierczak (1994). Comprehensive hydrochemical and sedimentological investigations of the lake were carried out by Kempe and co-workers (Kempe & Kazmierczak, 1990*a*, *b*, 1993; Kempe *et al.*, 1997). Indeed, the steep edge of the lake shows carbonate reefs (Fig. 9) that are composed of non-enzymatically precipitated carbonate and coralline red algae. Subfossil reef parts comprise a marine serpulite, followed by stromatolitic crusts composed of fibrous aragonite and microcrystalline laminae that encase former siphonocladalean green algae (Kempe & Kazmierczak, 1990*a*, *b*, 1993; Kazmierczak & Kempe, 1990, 1992; Kempe *et al.*, 1997). Younger parts and the living reef surfaces are essentially formed by squamariacean (*Peyssonnelia*) and corallinacean (*Lithoporella*) red algal crusts, nubecullinid foraminifera, and minor amounts of microcrystalline carbonate. Kempe & Kazmierczak (1990*a*, 1990*b*, 1993) and Kazmierczak & Kempe (1990, 1992) emphasized the participation of coccoid, pleurocapsalean cyanobacteria both in recent $CaCO_3$ precipitation and in the formation of subfossil stromatolites. In this paper we focus on observations based on samples taken during the dry season of 1993 and at the end of the wet season of 1996, and revise some of the previous interpretations with regard to cyanobacteria-associated calcification.

To clarify the identity of cyanobacteria, six morphotypes were cultivated. Their 16S rRNA genes were amplified from non-axenic cultures using cyanobacteria-specific primers. Phylogenetic analysis of 16S rDNA (G. Arp, G. Schumann-Kindel, W. Manz, U. Szewzyk & J. Reitner, unpublished data) revealed that two separate *Pleurocapsa* species are present, both related to other cyanobacteria of the *Pleurocapsa* group *sensu* Rippka *et al.* (1981). Two morphologically similar *Phormidium* strains are phylogenetically related to *Phormidium minutum*, but represent separate species. In addition, one species of *Calothrix* and one species of '*Oscillatoria*', which is related to '*Microcoleus* 10mfx', are present.

Reef surfaces between the seasonal minimal water level and 15 m depth are formed by living red algal thalli that are covered by an extensive green algal meadow (Kempe & Kazmierczak, 1993). Demosponges (*Laxosuberites* sp.) with internal gemmulae are abundant upon the red algal crusts and at the base of green algal tufts. Biofilms on the living red algae are thin (5–10 μm), discontinuous, and show patches of coccoid cyanobacteria. Besides pleurocapsalean cyanobacteria, large hemispherical cells (10–15 μm diameter) of an unidentified species ('*Dermocarpella*') are abundant (Fig. 10). $CaCO_3$ precipitates linked to cyanobacterial sheaths or biofilm EPS were not observed either in wet- or in dry-season samples. Below 15 m depth down to the chemocline at 23 m, red algal growth has ceased and reef surfaces are covered by 75–400 μm thick biofilms of filamentous cyanobacteria (*Phormidium*), diatoms and pleurocapsalean cyanobacteria. Trapped allochthonous $CaCO_3$ crystal aggregates and faecal pellets are common within the biofilms, but no autochthonous precipitation is evident.

Seasonally exposed reef tops (wet-season samples) show *Phormidium–Calothrix–Pleurocapsa* biofilms (Figs 11, 12) with scattered tufts of the green algal genus *Cladophoropsis*. The carbonate substratum rock (subfossil stromatolites) is heavily corroded by endolithic cyanobacteria of the *Hyella* morphotype. In contrast to the previously described biofilms, thin sections of the seasonally exposed reef tops show abundant, scattered $CaCO_3$ precipitates. Current precipitation is indicated by internal fibrous aragonite in dead cells at the base of living green algal tufts. Similar aragonite forms upon EPS-poor surfaces in voids in the reef rock framework. Within the biofilms microcrystalline $CaCO_3$ aggregates are concentrated at the interface with the liquid phase (Fig. 12). In addition, dissolution remnants, showing etched surfaces and truncated fabrics, occur throughout the biofilm. None of the precipitates is spatially linked to cyanobacterial sheaths, except for three observations of semitubular crystal aggregates that enclose middle parts of *Calothrix* trichomes (Fig. 11). Microcrystalline precipitates within *Pleurocapsa* colonies (between individual cells) were observed in two cases only.

In summary, non-enzymatically controlled $CaCO_3$ precipitation currently occurs in Lake Satonda, though to a very limited extent and restricted to reef tops and pore spaces. Photosynthetic CO_2 removal is apparently of secondary importance for precipitation, because precipitates are scattered throughout the biofilm EPS. In accordance with the case studies from Pyramid Lake and Lake Nuoertu, microcrystalline aggregates result from an EPS-mediated $CaCO_3$ precipitation where Ca^{2+} supply is sufficient in this alkaline, supersaturated setting. Consequently, the lack of Ca^{2+}-complexing exopolymers within lysed green algal cells results in rapid formation of fibrous aragonite fans. The restriction of non-enzymatically controlled precipitation to the reef tops results at least partly from a Ca^{2+} recycling by corrosion by endolithic cyanobacteria. At present, Ca^{2+} supply apparently does not exceed the amount of Ca^{2+} that can potentially be bound to the continuously produced exopolymer biomass (e.g. upon green algae, dead red algal crusts) at greater depth. Living calcareous red algae that withdraw Ca^{2+} enzymatically and suppress biofilm development on their surfaces might be crucial in explaining the lack of extensive EPS-mediated calcification in Lake Satonda.

Discussion

From biomineralization processes in higher plants and animals (Addadi & Weiner, 1989; Mann, 1989; Simkiss & Wilbur, 1989), and from the acidic nature of biofilm exopolymers, it is reasonable to infer that cyanobacterial sheaths and cyanobacteria-dominated biofilms act in general as agents that inhibit rather than promote $CaCO_3$ precipitation at first (see also the concept of 'organomineralization': Trichet & Defarge, 1995). As a principle,

several steps of non-enzymatically controlled $CaCO_3$ precipitation have to be distinguished. These are the physicochemical prerequisites/framework for precipitation (i.e. carbonate equilibrium in the macro- and microenvironment), and seed crystal formation and growth.

In general, calcification of cyanobacterial biofilms is restricted to supersaturated environments. $CaCO_3$ minerals nucleate (in contrast to e.g. gypsum) only at a considerable supersaturation (Kelts & Hsü, 1978; Kempe & Kazmierczak, 1990*b*). In a comparative study Kempe & Kazmierczak (1990*b*) suggested that a minimum of approximately 6.3-fold calcite supersaturation is necessary for $CaCO_3$ precipitation associated with cyanobacterial mats of stromatolites. In contrast, enzymatically controlled biomineralization (e.g. in Coccolithophoridae, molluscs) occurs also in less supersaturated or even undersaturated environments. Additionally, the presence of inhibitors (such as Mg^{2+}, SO_4^{2-}, PO_4^{3-}, fulvic and humic acids, citric acid) have to be taken into account to explain supersaturation levels as observed in nature (Berner *et al.*, 1978; Kelts & Hsü, 1978; Trichet & Defarge, 1995).

Given a high pH and a high carbonate alkalinity, CO_2 fixation (and respiration) by bacteria and cyanobacteria are presumably factors with negligible influence on the carbonate equilibrium. Observations and arguments that support this interpretation are as follows: (1) $CaCO_3$ precipitates in biofilms of lakes of high alkalinity are not spatially linked to cyanobacteria or to any other living photosynthetic organism, but are randomly distributed within the EPS and at places free of or poor in biofilms. In a similar way Braithwaite & Zedef (1996) argued that photosynthesis alone is insufficient to cause hydromagnesite precipitation ($Mg_5[OH/(CO_3)_2]_2 \cdot 4H_2O$) in biofilms of soda lake stromatolites in Salda Gölü, Turkey. (2) From a theoretical point of view the removal of a given amount of inorganic carbon (e.g. a net removal of the order of 200–400 μmol l^{-1} is observed in marine settings during high productivity) from moderately to highly alkaline waters (e.g. Pyramid Lake and Lake Nuoertu mixing zone waters) does not raise supersaturation significantly under present-day atmospheric conditions. In contrast, the causal relationship of photosythetic CO_2 removal and calcium carbonate mineral precipitation has been shown conclusively for less buffered settings such as hardwater lakes and swamps (e.g. Kelts & Hsü, 1978; Thompson & Ferris, 1990; Merz, 1992; Thompson *et al.*, 1997). On the basis of both points it is reasonable to question the effectiveness of photosynthetic CO_2 removal in causing $CaCO_3$ precipitation in these alkaline lakes and mixing zone environments. However, final evidence for this interpretation can only be inferred from laboratory experiments under controlled conditions.

On the other hand, Ca^{2+} supply should be the limiting factor in such environments, both in enhancing supersaturation and with regard to mass balances. At high pH, the attraction and spatial concentration of Ca^{2+} by the acidic groups of exopolymers should be most effective. Heterogeneous nucleation at sheath polymers is energetically more favourable than homogeneous nucleation, which in any case is unlikely to occur in nature (Stumm, 1992). Experiments in biomineralization have shown that Ca^{2+} complexing of acidic macromolecules temporarily inhibits nucleation despite a sufficient Ca^{2+} supply (Wheeler & Sikes, 1989). Mineralization is only promoted by some acidic organic substances after they have undergone conformational changes due to adsorbtion to solid substrata. Therefore, prior to Ca^{2+} saturation of binding sites, no nucleation occurs. Given continuous $CaCO_3$ supersaturation, nucleation starts after Ca^{2+} saturation of the highly disordered exopolymers at places of Ca^{2+} binding sites that are 'by accident' suitably arranged. Random distribution of potential nucleation sites may account for the observation that precipitates are randomly distributed within the EPS. Scarce observations of $CaCO_3$ precipitates directly linked to cyanobacteria suggest compositional differences of their EPS and consequently different susceptibility for calcification under the given, alkaline conditions.

Heterotrophic bacteria affect the Ca^{2+} complexation by their own EPS secretion. Some species thrive directly on the EPS produced by cyanobacteria, i.e. they exoenzymatically cleave and decarboxylate the polymers. This defunctionalization may cause a breakdown of Ca^{2+} binding capacity and secondary Ca^{2+} release. CO_2 liberation by respiration should be ineffective in lowering pH in a well-buffered highly alkaline milieu.

In summary, in moderately to highly alkaline settings the main influence of cyanobacterial activity on $CaCO_3$ precipitation is supposed to be via the production of extracellular polymeric substances (EPS). EPS, above all acidic polysaccharides, act as a Ca^{2+} 'buffer'. They attract divalent cations, thereby preventing precipitation at first. From this viewpoint, primarily produced polysaccharide sheaths of cyanobacteria can be regarded as rather unsuitable nucleation sites for calcium carbonate minerals. The Ca^{2+}-binding capacity of EPS can be exceeded by a continuous Ca^{2+} supply and/or by secondary Ca^{2+} release during exoenzymatic degradation which in turn reduces the binding capacity itself. Overall, these processes are considered to be responsible for the delayed onset of precipitation near acidic groups that are suitably arranged 'by accident'. The random distribution of the resulting microcrystalline precipitates together with the lack of evidence for a spatial relationship with cyanobacterial cells suggests that the effect of photosynthetic CO_2 fixation in raising supersaturation is of secondary importance. Consequently, in moderately to highly alkaline settings, calcification in cyanobacterial biofilms occurs in cases of unsuccessful inhibition.

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